EFFECT OF LANTHANUM DOPANT ON THE PROPERTIES OF $CaCu_3Ti_4O_{12}$ THIN FILMS SYNTHESIZED BY SOL-GEL METHOD

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by

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DECLARATION

I hereby declare that I have conducted, completed the research work and written the dissertation entitled "Effect of Lanthanum Dopant on the Properties of $CaCu_3Ti_4O_{12}$ Thin Films Synthesis by Sol-Gel Method". I also declare that it has not been previously submitted for the award of any degree or diploma or other similar title of this for any other examining body or University

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Date:

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ABSTRAK

$CaCu_3Ti_4O_{12}$ (CCTO) diketahui mempunyai pemalar dielektrik yang tinggi iaitu $\varepsilon \sim 10^4$ pada frekuensi yang rendah. CCTO tulen dan CCTO filem nipis yang didop dengan La disediakan melalui kaedah sol-gel. Bahan mentah iaitu $Ca(CH_3COO)_2$, $Cu(C_2H_3O_2)_2.H_2O$, $Ti[OCH(CH_3)_2]_4$ telah digunakan untuk menghasilkan filem nipis CCTO tulen manakala $La(NO_3)_3.6H_2O$ telah digunakan sebagai sumber dopan untuk menghasilkan La terdop CCTO ($Ca_{1-x}La_xCu_3Ti_4O_{12}$) dengan x = 0, 0.01, 0.02, 0.05 and 0.10. Larutan sol-gel dipanaskan selama dua jam setengah pada suhu 110 °C dan dimendapkan ke atas Si wafer jenis p menggunakan kaedah salutan berputar. Selepas itu filem nipis yang telah dikeringkan disepuhlindap menggunakan dua peringkat penyepuhlindapan pada suhu 500 °C selama 10 minit dan 900 °C selama 1 jam. Pembentukan fasa CCTO di ditentukan dengan menggunakan pembelauan sinar-X (XRD) dan mikrostrukturnya diperhatikan melalui mikroskop imbasan electron pancaran medan (FESEM). Elemen komposisi CCTO filem nipis yang disediakan dikenal pasti menggunakan serakan tenaga sinar-X (EDX). Topografi dan fasa pengimejan sampel diperolehi menggunakan mikroskop daya atom (AFM) dengan mengimbas kawasan seluas 10 μm x 10 μm. Penganalisis parameter semikonduktor (SPA) digunakan untuk mengukur cirri-ciri arus-voltan (I-V) dan kapasitan-voltan (C-V). Sampel disalut dengan elektrod perak untuk pengukuran sifat-sifat elektrik dan dielektrik. Pembentukan sebatian CCTO disahkan melalui XRD dengan beberapa puncak kecil CuO dan TiO_2 wujud bersama-sama dalam CCTO filem nipis. Saiz butiran adalah diantara 38 nm hingga 205 nm yang diukur oleh SEM. EDX analisis mengesahkan kehadiran elemen

kimia CCTO di dalam filem nipis. Analisis AFM menunjukkan tiada kewujudan fasa kedua daripada pengimejan fasa di permukaan filem. Sampel didop dengan 2 at% La memberikan kekonduksian elektrik yang lebih baik. Didapati bahawa dopan La memberikan peningkatan ke atas sifat dielektrik CCTO dimana 2 at% La memberikan nilai dielektrik yang optimum.

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ABSTRACT

The $CaCu_3Ti_4O_{12}$ (CCTO) was discovered to possess high dielectric constants, ε ~ 10^4 at low frequencies. The undoped and La doped CCTO thin films were prepared by sol-gel method. The raw materials of $Ca(CH_3COO)_2$, $Cu(C_2H_3O_2)_2.H_2O$, $Ti[OCH(CH_3)_2]_4$, were used to produce undoped CCTO thin films, whereas $La(NO_3)_3.6H_2O$ was used as dopant source to form La-doped CCTO ($Ca_{1-x}La_xCu_3Ti_4O_{12}$) with x = 0.01, 0.02, 0.05 and 0.10. The sol-gel solution was heated for two and half hours at 110 °C and then deposited on the p type Si wafer using spin coating process. The dried films were annealed using two stages of annealing process at 500 °C for 10 minutes and followed by at 900 °C for 1 hour. The phase formation of the CCTO was identified by X-ray diffraction (XRD) and the microstructure observed by field emission scanning electron microscope (FESEM). The elemental composition of prepared CCTO thin films was identified by using energy dispersive X-ray (EDX). The topography and the phase imaging of the samples were obtained using atomic force microscopy (AFM) by scanning area of 10 μm x 10 μm. The semiconductor parameter analyzer (SPA) was used to measure the current-voltage (I-V) and capacitance-voltage (C-V) characteristics. The samples were coated with silver electrodes for electrical and dielectric properties measurement. The formation of CCTO compound was confirmed by XRD with some minor peaks of CuO and TiO_2 co-exist in CCTO thin films. The grains size is in between 38 nm to 205 nm measured by SEM. The EDX analysis confirmed the chemical element of CCTO exist in the thin films. The AFM analysis confirmed no

significant secondary phase observed from the phase imaging of the film surface. Sample doped with 2 at% La give better electrical conductivity. The La dopant shows improvement on the dielectric properties of the CCTO with 2 at% La give optimum dielectric value.

CHAPTER 1

INTRODUCTION

1.1 Introduction

Nowadays, there is an increasing demand on dielectric materials which have high dielectric constant to surpass their present abilities to be of use in the fast changing world of electronic devices (Saji et. al., 2009). Ceramic materials also can be used in the microelectronic industries as dielectric substrate due to their good dielectric properties, high integration potential, high reliability, excellent thermal conductivity and also their thermal expansion efficient close to silicon (Stiegelschmitt et. al., 2004). In particular, one of the members, $CaCu_3Ti_4O_{12}$ (CCTO) was recently studied to investigate the origin of this compound and also its dielectric properties for single crystal, powders and thin films. High dielectric constants allow smaller capacitive components, thus offering the opportunity to decrease the size of electronic devices. The dielectric constant for the dielectric materials seems will be affected by the frequency used to it. This CCTO material also seems promising for low frequency microelectronic applications like decoupling capacitors. Miniaturization of capacitors demands greater volumetric efficiency of capacitance through material which has higher permittivity. These capacitors also have to be stable over a wide range of temperature and operating voltages. Since the capacitance is proportional to the dielectric constant, high dielectric constant of the materials is desired. It is also desirable to have the loss or dissipation factor as small as possible. Moreover, it been reported by Sulaiman et al. (2010) that the CCTO materials seem to be promising also for high frequencies

application in range of few hundred MHz to GHz like devices for wireless communication.

The huge dielectric constant (ε) of perovskite type oxides (ABO_3) of non-ferroelectric $CaCu_3Ti_4O_{12}$ oxide over a wide range of temperature and frequency recently attracted much scientific attention. This makes CCTO has potentially useful for important applications in microelectronics and memory devices. According to Subramaniam et al. (2000) this oxide belongs to a family of oxides of the type $ACu_3Ti_4O_{12}$and $ACu_3Ti_3FeO_{12}$ (A = metal ion) and was studied nearly 30years ago since 1979 (Jha et. al., 2003). Based on the study, $CaCu_3Ti_4O_{12}$ possesses a distorted cubic perovskite (ABO_3) structure with the space group Im3 and a lattice parameter of 7.391 Å (Bochu et. al, 1979).

The unusually high dielectric constant $\varepsilon \sim 10^4$ of CCTO at low frequencies remains almost constant between 100 and 600K with no structural phase transition (Brize et. al., 2006). Further study by (Ramirez et. al., 2000) confirmed the nearly stable dielectric constant in the temperature range of 100 – 400K. Usually, some materials with dielectric constants higher than 1,000 are associated with ferroelectric properties and the dielectric constant changes greatly during the ferroelectric phase transition. Materials without phase transition is exactly what we need while constructing microelectronic devices. The phase transition imposes an unfavorable characteristic of a strong temperature dependence of the dielectric constant that is incompatible with many electronic applications. Like ferroelectrics, its show a great enhancement in permittivity nears its Curie point (which is typically associated with a change in crystal structure). The ferroelectric behavior is

attributed to the appearance of a spontaneous polarization that is tied to a structural phase transition. This spontaneous polarization is realized in the characteristic hysteresis loop and can be reversed by the application of the electric field to the opposite direction. The fact that the ferroelectric phenomenon occurs only in a class of materials possessing a non-centrosymmetric crystal structure and a polar axis has attracted great interest in $BaTiO_3$ which has and other ferroelectrics having ABO_3-type perovskite structures (Lines and Glass, 1977).

It is often required that the dielectric constant of the material is fairly independent of the temperature for industry application. Therefore CCTO, with its low dependence on temperature, is of great interest to us. Saji and Han, (2009), reported that dielectric constant of CCTO is stable and has no phase transition of CCTO in the temperature range of 100 to 600K. Moreover, CCTO was also discovered to possess the largest ε, i.e. 80,000 for single crystal and 10,000 for bulk material at room temperature. The higher ε, the more charge it can store, and the smaller electronic circuits can be designed. Unlike most dielectric materials, $CaCu_3Ti_4O_{12}$ retains its enormously high ε over a wide range of temperatures (−173 to 327 °C), making it ideal for a wide range of applications (Mohamed et. al., 2007).

However, further research on its dielectric properties indicates that this material has a high dielectric loss, which seriously blocks its practical application. Unfortunately, the CCTO loss tangent of ~0.15 is high for present ceramic application requirement (Smith et. al. 2009). The dielectric loss mechanism is the

resonance of electric dipoles in the atom or molecule of the material. The controversy surrounding the origin for the giant dielectric constant has not yet been put to rest. Research indicates that $CaCu_3Ti_4O_{12}$ may be part of a new class of oxide perovskites whose high dielectric properties are different than classic ferroelectric. It is necessary to know the origin of dielectric loss in CCTO ceramics to find an effective method to lower it. It also has been reported that the dielectric properties of CCTO are sensitive to its microstructure which depends upon the processing conditions such as annealing duration, annealing temperature, dopant and etc.

There have been also many hypotheses since the original finding for the origin of the abnormally high dielectric constant of CCTO over the vast temperature range. According to Prakash and Varma (2007) the dielectric constant of CCTO increased drastically with increase sintering temperature and duration as a consequences change in the microstructural and compositional heterogeneity.

Moreover, there have been a number of studies about the doping effects on the dielectric properties in this material such as Cr_2O_3 doped CCTO, Mn doped CCTO, ytrrium doped CCTO, boron doped CCTO and others. It is necessary to know the origin of dielectric properties in CCTO material to find an effective method to enhance these properties. All these studies mentioned herein aimed to improve the dielectric property of the CCTO material by controlling the chemistry and structure of interfacial regions at grain boundaries. In overall, this research is more focusing on the dielectric properties of CCTO compound with additional dopant. The addition of dopant may affect the microstructure formation of CCTO and hence may alter its dielectric properties. The studies in this research will be focusing more

on the La doped CCTO ($Ca_{1-x}La_xCu_3Ti_4O_{12}$). In this study the La^{3+} ion is expected to substitute the Ca^{2+} ion of the CCTO material. The dopant that will be used is this research is Lanthanum Nitrate Hexahydrate, $La(NO_3)_3.6H_2O$. In this project, different amount of La is used to observe the effect of these dopants on CCTO dielectric properties. Perhaps the additional of La incorporate into this CCTO material can enhance the dielectric property of CCTO. It is expected that the La-doped CCTO ceramics will have outstanding electrical properties for practical applications.

1.2 Problem Statement

As mentioned earlier, it was found that CCTO has very high dielectric constant which exhibits an extraordinary high dielectric constant up to 10^4 having potential to use in miniaturized devices. CCTO has stable dielectric constant between 100 K and 600 K with no phase transition. Materials with excellent dielectric properties is what we need while constructing the microelectronic devices. Doping of CCTO material is one of the important techniques to improve the dielectric properties to obtain required characteristics for different applications such as in antenna and wireless communication. To improve the dielectric constant of the CCTO material, we proposed to dope the CCTO with different amount of La in order to study on how the addition of La dopant will affect the dielectric properties of the CCTO thin films. La^{3+} ions (1.15Å) have nearly the same radius as Ca^{2+} ions (1.05Å) and are much larger than Cu^{2+} ions (0.73Å), hence it prefers to enter into Ca sites rather than into Cu sites to form either La doped CCTO. Rai et al, (2009) reported that introduction of La^{3+} into CCTO increased the dielectric constant of the CCTO

which is suitable for the microelectronic devices application. Jin et al., (2009) was also reported that the high dielectric constant could be significantly enhanced up to >25000 by La-dopant in the classic ceramic $BaTiO_3$ system.

Generally, the CCTO is usually produced by conventional solid state method. Many researchers are working for the development of CCTO compound which will provide enhanced dielectric constant. The sol-gel method seems to be promising to be used in order to overcome the limitations of the conventional solid state reaction such as non-homogenous mixing, high processing temperature, long reaction times up to 8 hours and higher cost (Bender and Pan, 2005). A sol–gel process has shown considerable advantages, including excellent chemical stoichiometry, compositional homogeneity and lower crystallization temperature due to the mixing of liquid precursors on the molecular level as compared with other process (Ramirez et al., 2011). Ion diffusing displacement is shortened in sol–gel process. Other than that, Jin et al., (2007) have synthesized the giant dielectric constant material CCTO by sol–gel method and it was found that the dielectric permittivity of CCTO synthesized by sol–gel method was found three times larger than solid-state reaction method.

1.3 Objective

A study will be undertaken to accomplish the following objectives:

- To fabricate and study the effect of the undoped and La doped CCTO thin film by sol gel method.
- To investigate and study the properties of fabricated undoped and La doped CCTO thin films by using different amount of doping concentration of x = 0.00, 0.01, 0.02, 0.05, and 0.10 (phase formation, microstructure, morphology, electrical and dielectric properties).

1.4 Project Approach

The $CaCu_3Ti_4O_{12}$ (CCTO) compound has recently attracted considerable research interest due to its unusually high and weakly temperature dielectric permittivity reported by many researchers. To further explore its unusual dielectric phenomena, the current study focuses on the effect of the different amount of La dopant on the properties of CCTO. Doping method opens an effective way to alter the dielectric performance, both high dielectric constant (ε) and low dielectric loss (tan δ) essential for capacitance application. For the doping study, five different amounts of La dopant were selected to form La doped CCTO ($Ca_{1-x}La_xCu_3Ti_4O_{12}$) with x = 0.00, 0.01, 0.02, 0.05, and 0.10.

In electronic industry, the fabrication of the thin films has the benefits over the bulk material as it has a smaller footprint, lower power requirements and also faster response time. In this project, the CCTO thin films was fabricated by using the sol

gel method as it offers the ability to coat complex and large area substrate, homogenous distribution of elements, and ease of compositional control and can obtain the high purity of material.

1.5 Scope of work

The effect of different amount of La as dopant on the properties of CCTO thin films is studied in this project. The raw materials which are used are calcium acetate, $Ca(CH_3COO)_2$, copper acetate, $Cu(C_2H_3O_2)_2.H_2O$, titanium(IV) isopropoxide, $Ti[OCH(CH_3)_2]_4$, lanthanum nitrate hexahydrate, $La(NO_3)_3.6H_2O$ (dopant). The three main precursors of CCTO which are $Ca(CH_3COO)_2$, $Cu(C_2H_3O_2)_2.H_2O$, and $Ti[OCH(CH_3)_2]_4$ were mixed together in the mole ratio of 1:3:4. The addition of La dopant are added according to the mol fraction of x = 0, 0.01, 0.02, 0.05 and 0.10. The thin film of CCTO is fabricated by using the sol gel synthesis technique which consists of dissolved all precursors material into acetic acid, heating with continuous stirring, spin coating, drying and annealing of the samples. The samples is annealed by using two step of annealing which is at 500 ^oC for 10 minutes and 900 ^oC for 1 hour with heating rate of 10 ^oC/min. The samples were investigated using X-ray diffraction (XRD) to examine the phase present, field effect scanning electron microscopy (FESEM) to analyze the microstructure, energy dispersive X-ray (EDX) to determine the chemical compositions present, atomic force microscopy (AFM) to analyze the surface topography, current voltage (I-V) characterization to measure the electrical properties and capacitance voltage (C-V) characterization to measure the dielectric properties.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

This chapter consists of some information and theories which is related to this research of $CaCu_3Ti_4O_{12}$ (CCTO). In general, CCTO is one of the special electro-ceramics materials which have very high dielectric constant over wide temperature and frequency. Further study of CCTO is being made in order to observe the dielectric properties of CCTO by additional doping on CCTO. A few of experimental methods and theoretical reason are discussed to explained the behavior of the perovskites ABO_3 where A and B are cations.

2.2 Electro-ceramic Materials

Ceramic materials that have been specially formulated for specific electrical, magnetic, or optical properties are commonly known as electro-ceramics material. Their properties can be tailored to operation as insulator, highly conductive ceramics, ferroelectric materials and the others. One of the electro-ceramic materials which are suitable for capacitor application is CCTO. Ceramic materials that are good electrical insulators are referred to dielectric materials. Dielectric can be defined as materials with high electrical resistivity (Moulson and Herbert, 2003).

Unlike normal dielectric materials with dielectric constants lower than 100, certain types of crystals with a nonsymmetrical structure exhibit high dielectric

constants as high as 10^5 in specific conditions (Kao, 2004). Most materials in this category are ferroelectric crystals, and their ferroelectric behavior is attributed to the appearance of a spontaneous polarization that is tied to a structural phase transition. Materials exhibiting ferroelectric properties possess reversible spontaneous polarization. This spontaneous polarization is realized in the characteristic hysteresis loop and can be reversed by the application of the electric field to the opposite direction.

The dielectric materials have important properties that are useful in capacitors application. Dielectrics in capacitors serve three purposes which are:

- To keep the conducting plates from coming in contact, allowing for smaller plate separations and therefore higher capacitances;
- To increase the effective capacitance by reducing the electric field strength, which means the same charge at a lower voltage; and
- To reduce the possibility of shorting out by sparking (more formally known as dielectric breakdown) during operation at high voltage.

The perovskites, ABO_3 are the most important class of dielectric materials. According to Khalil and Hammad (2002), oxides with the perovskite structure are well known for their ability to produce high dielectric constants with ferroelectric property. A perovskite compound (ABO_3) consists of an alkaline earth metal (denoted by A), a transition metal (denoted by B) and oxygen to form the oxide (denoted by O). Moreover, Sanchez-Benitez et al., (2004), reported that there are many materials that have perovskite structure including $MgTiO_3$, $PbTiO_3$, $CaTiO_3$, and $BaTiO_3$. $CaCu_3Ti_4O_{12}$ (CCTO) is one of the well known perovskite material.

The unusual dielectric behavior of the perovskite material of CCTO has attracted some much attention due to it has very high dielectric constant. Typically, perovskite is the mineral name of calcium titanate ($CaTiO_3$). Its simplest structure is cubic, which is the high temperature form for many mixed oxides of the ABO_3 type. The simple cubic structure consists of corner sharing oxygen octahedra (BO_6) arranged in three dimensions with smaller, highly charged cations (B: Ti^{4+}, Zr^{4+},Sn^{4+},Nb^{5+},Ta^{5+},W^{6+}, etc.) located in the middle of the octahedra, and lower charged, larger cations (A:Na^{+}, K^{+}, Ca^{2+}, Ba^{2+}, Pb^{2+}, etc.) in between the octahedra (Xu, 1991). The ideal perovskite structure is shown in Figure 2.1.

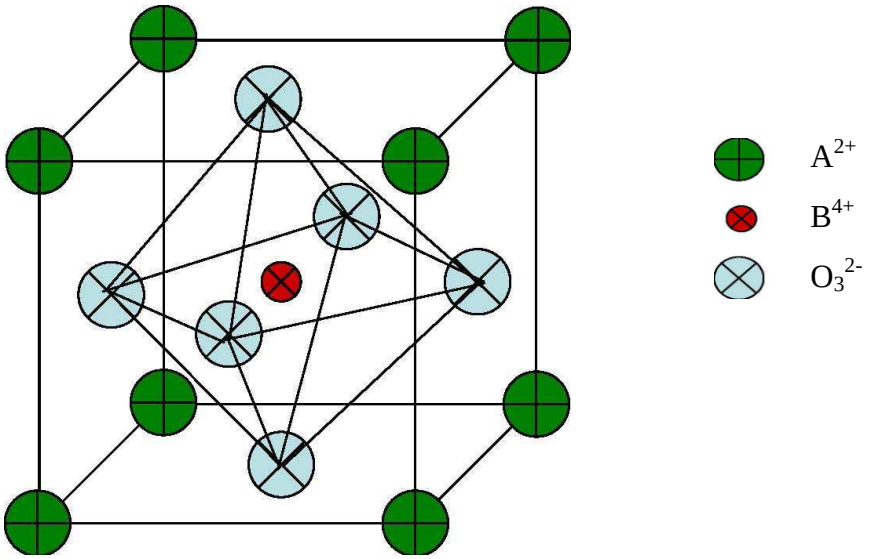

Figure 2.1: An ideal cubic ABO_3 perovskite-type unit cell (Sebastian, 2008).

The perovskite structure can be also regarded as a cubic close-packed arrangement of large A and O ions with smaller B ions filling the octahedral interstitial positions. The structure is also very tolerant to cation substitution to both A and B sites of lattice, and hence may lead to more complex compounds, such as

$(K_{1/2}Bi_{1/2})TiO_3$,$Pb(Fe_{1/2}Ta_{1/2})O_3$, $Pb(Co_{1/4}Mn_{1/4}W_{1/2})O_3$, $Pb(Mg_{1/3}Nb_{2/3})O_3$, and $Pb(Zn_{1/3}Nb_{2/3})O_3$ (Xu, 1991).

2.3 Dielectric Properties

A dielectric can be defined as material any material placed between the plates of a capacitor for examination by an applied electric field (Grimnes and Martinsen, 2008). As discussed in the previous section, it is known that the ceramic materials are good electrical insulator which is referred as dielectric materials. Although these materials do not conduct electric current when an electric field is applied, they are also not inert to the electric field. The field causes a slight shift in the balance of charge within the material to form an electric dipole, thus the source of the term ‘dielectric’.

Dielectric material may be polarized by the action of an applied electric field. When dielectric is placed in electric field, electric charges do not flow through the material, as in conductor, but only slightly shift from their average equilibrium positions causing dielectric polarization. These materials have positive charges are displaced along the field and negative charges shift in the opposite direction. Although the dielectric materials are poor conductor of electricity, it is an efficient supporter of electrostatic field. An electrostatic field can store energy if the flow of current between opposite electric charges poles is kept to minimum while the electrostatic lines of flux are not impeded or interrupted (Gupta, 2011).

Another important property of dielectric materials is its ability to support an electrostatic field while dissipating minimal energy in the form of heat. The lower the dielectric loss which is proportion of energy lost as heat, the more effective is a dielectric material. Another consideration is the dielectric constant, the extent to which a substance concentrates the electrostatic lines of flux. Dielectrics fulfill circuit functions for which their dielectric constant, ε that is directly proportional with the capacitance and also the dissipation factors, tan δ. These parameter is one of the primary importance's which will affect the properties of dielectric materials as stated above. Properties below demand careful consideration in certain application of dielectric which is:

i) Capacitance

ii) Loss tangent

2.3.1 Capacitance

The capacitance is an important characteristic of dielectric materials. The capacitance of the material is the relationship between the charge put on the material and its potential energy (Leret et al., 2007). Capacitance is the ability of a circuit system to store charge and a capacitor is a device in an electric circuit for storing electrical charge. It is also a measure of the amount of electric charge stored (or separated) for a given electric potential (Carr, 2002). A common form of charge storage device is a two-plate capacitor. If the charges on the plates are +Q and –Q, and V give the voltage between the plates, then the capacitance is given in Equation 2.1.

$$C = Q/V \tag{2.1}$$

The SI unit of capacitance is the farad; 1 farad = 1 coulomb per volt.

Other than that, the basic formula for the capacitance of a parallel-plate capacitor also can be given by:

$$C = \frac{\varepsilon_o \varepsilon_R A}{t} \tag{2.2}$$

Where ε_o is the relative permittivity of free space, 8.85 x 10^{-14} F/cm, and ε_r is the permittivityof the material. A is the area of the each plate and t is the thickness of the capacitor. Therefore the capacitance is a function of the material, and also the geometry of the device. The capacitance can be calculated if the geometry of the conductors and the dielectric properties of the insulator between the conductors are known. ε_r is more often used to describe dielectric properties. In addition, the dielectric constant, ε_r is independent of the material's thickness. A material with a higher dielectric constant is desired when making capacitor devices.

2.3.2 Loss Tangent

A lower loss tangent yields a better capacitor and the loss tangent is measured as a percent. Since every capacitor is not created the same, the loss tangent can be used to characterize the dielectric material. Some energy is lost in real capacitors, however. These losses may be due to resistance losses or dielectric losses. Resistance losses are electrical energy transferred to heat due to current flowing

through the leads and plates of the capacitor. Dielectric losses occur due to heat produced during the change in the molecular structure of the dielectric due to the changes in polarity (Fowler, 1999). The loss tangent can change with each capacitor and may be independent of the processing condition. The loss tangent (or dissipation factor) will show the dielectric performance via energy loss. For a lossy (imperfect) dielectric the dielectric constant can be represented by a complex relative dielectric constant in Equation 2.3.

$$\varepsilon = \varepsilon' - i\varepsilon'' \tag{2.3}$$

ε’ = real part of dielectric constant

ε’’= imaginary part of dielectric constant

The small difference in phase from ideal behavior is defined by an angle δ, defined through the Equation 2.4.

$$\frac{\varepsilon''}{\varepsilon'} = \tan\delta \tag{2.4}$$

Tan δ = the loss tangent or dissipation factor

ε" = the loss factor

Loss tangent can be used to determine the capacitor quality. The loss tangent is also used to measure the efficiency of the capacitor and the “Q” or quality factor is the reciprocal of loss tangent and is sometimes used to describe the dielectric’s characteristics. Based on previous research by Ramirez, et. al., (2000) the dielectric constant and loss component (tan δ) for two different samples of CCTO are shown as a function of temperature at a frequency of 1 kHz, in Figure 2.2.

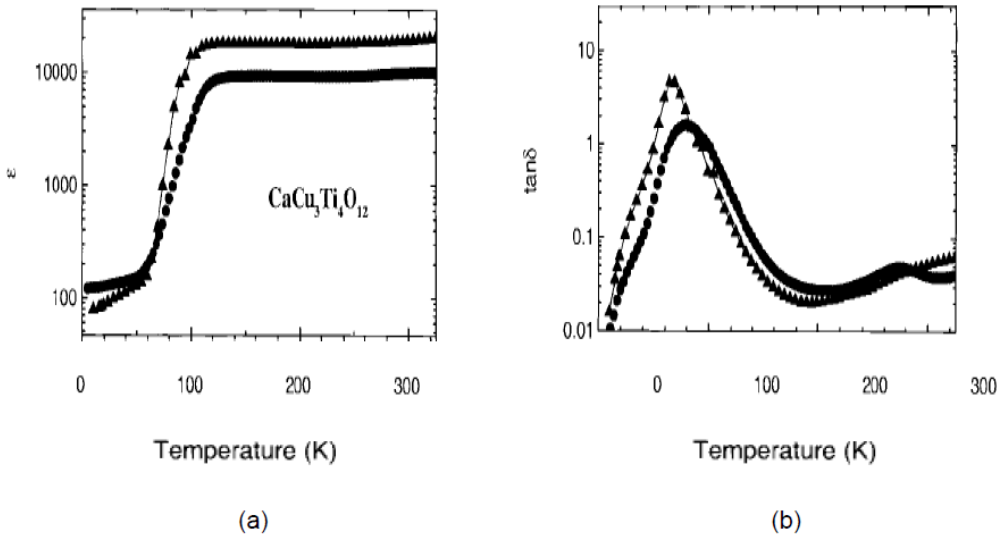

Figure 2.2: (a) The real part of the dielectric constant, ε (T), for two different samples of CCTO. (b) The loss component of the dielectric response, expressed as tanδ (Ramirez, et. al., 2000).

Ramirez et. al. in 2000 reported that the large value of dielectric properties of CCTO are depending on the grain boundary, the presence of twin boundaries, planar defects and displacements of Ti ions. The dielectric constant for CCTO decreases with increasing frequency, to a value of 9200 at 1MHz due to restricted movement of the dipole charges with increasing rate of electric field.

2.4 $CaCu_3Ti_4O_{12}$ Compound

Bulk CCTO compound which is usually prepared by conventional solid state method normally is a mixture of three types of starting materials which are $CaCO_3$, TiO_2 and CuO (Mohamed et al., 2007). The reaction takes place between these raw materials as shown in Equation 2.5.

$$CaCO_3(powder) + 3CuO\ (powder) + 4TiO_2(powder) \longrightarrow CaCu_3Ti_4O_{12}(powder) + CO_2(gas)\uparrow \quad (2.5)$$

However, Ramirez et al. (2011) reported that the films have an advantage over bulk materials and there are few attempt made to grow the CCTO thin films on various substrates for future application in microelectric devices. The soft chemical method or sol gel method has been widely used to prepare the CCTO based thin films (Li et al., 2009; Ramirez et al., 2011). In this research, the CCTO compound for thin films is a mixture of three types of starting materials which are calcium acetate, copper acetate and titanium (IV) isopropoxide using the sol gel synthesis technique. The reaction take place between these raw materials as shown in Equation 2.6.

$$CaC_4H_6O_4\ (\text{calcium acetate}) + 3\ CuC_4H_6O_4H_2O\ (\text{cupric acetate}) + 4\ TiC_{12}H_{28}O_4\ (\text{titanium (IV) isopropoxide}) \longrightarrow CaCu_3Ti_4O_{12}\ (\text{CCTO}) \quad (2.6)$$

*note that by product of the reaction is ignored

According to Brize et al. (2006), the CCTO was first synthesized by Bochu et al. (1979). The CCTO has distorted, complex cubic perovskite like structure with *Im3* space group and lattice parameter, a=7.391Å (Saji and Choe, 2009; Kwon et al., 2008; Leret et al, 2007). The TiO_6 octahedra are tilted, resulting in the doubling of the perovskite-like lattice parameter and involves a square planar arrangement of the oxygen around the Cu^{2+} cations. Like in the perovskite, the Cu^{2+}cations have 12 nearest-neighbor oxygen atoms but the isocahedronis slightly distorted (Brize et al., 2006). The extended unit cell structure of $CaCu_3Ti_4O_{12}$ is shown in Fig. 2.3. Here,

the Ca^{2+} ions occupy the corners and the center of the unit cell while Cu^{2+} ions are located on the centers of cell edges and planes. The Ti^{4+} ions are surrounded by 6 oxygen ions, forming TiO_6 octahedra which are tilted inward in order to make a square planar arrangement for the nearby Cu^{2+} ions (Subramaniam et al., 2000).

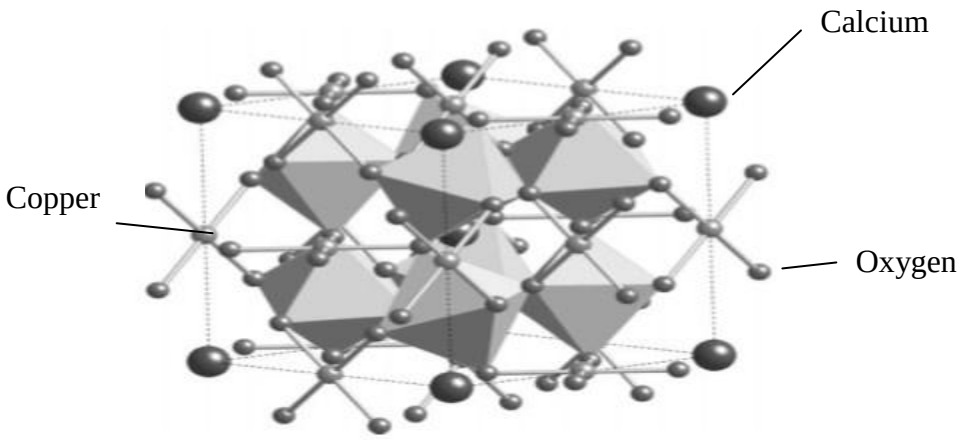

Fig. 2.3: Three-dimensional unit cell structure of $CaCu_3Ti_4O_{12}$.

From Figure 2.3, structure of CCTO shown as TiO_6 octahedron, oxygen atoms are showed as small sphere attached to copper atoms which are at the centre of the plane, and big spheres of calcium atoms at the edge and at the centre of the structure. In 2000, Subramaniam et al. have reported that CCTO has large dielectric constant, and that CCTO experienced no ferroelectric phase transition down to 35K. CCTO remains its structure down to 35K which has been examined by neutron powder diffraction. This behavior differs from other ferroelectric materials, such as $BaTiO_3$. While constructing microelectronic devices, materials without phase transition is exactly what we need.

Subramanian et al. (2000), also mentioned that the enhanced polarizability and the dielectric constant in $CaCu_3Ti_4O_{12}$ could be due to the tension of the Ti-O

bonds and that the extreme tilt of the TiO_6octahedra prevents the formation of the ferroelectric state. Although the high dielectric constant in CCTO can be explained from the structural point of view, there have been many reports that strongly indicate that the other mechanisms are possible.

2.5 Synthesis of $CaCu_3Ti_4O_{12}$

The dielectric properties of CCTO seem to be depends on their processing condition. The conventional solid state reaction method is the most widely used techniques to form the CCTO materials. Other than that, there are also a few methods that can be used to synthesis the CCTO materials such as by using the microwave heating, co-precipitation method, wet-chemical synthesis method and also the sol gel method (Yu et al., 2008; Zhao et al., 2012).

For $CaCu_3Ti_4O_{12}$ synthesized by using conventional solid state method, Bender and Pan (2005), examined the effects of the processing conditions in detail by using various conditions including the powder mixing, firing temperature (both calcination and sintering), and annealing. Its revealed that increasing sintering temperature in the range from 990^{o}C to 1050^{o}C led to increase in both dielectric constant (714 to 82,450) and loss (0.014 to 0.98) accompanied by milling method (Bender and Pan, 2005). They suggested that the improved dielectric constant can be attributed to the higher concentration of defects in the grain core. Also, they explained the sensitivity of the dielectric properties to the processing from the changes in the resistivity of grain boundaries.

Other than that, the method of pre-sintering process followed by the microwave heating has been claimed can enhance the dielectric properties of the CCTO materials. Hutagalung et al. (2008) reported that by using the microwave method, better dielectric properties can be obtained which is suggested to be due to a better microstructure densification as the densification increases the grain size and decreases the grain boundaries. This phenomenon will lead to an increase in the dielectric constant and dielectric losses of the CCTO.

Barbier et al. (2009) had discussed the CCTO materials prepared by using soft chemistry method of co-precipitation between CCTO pellets and thick films. By using the metal chlorides materials as precursors, they can obtained very high value of dielectric constant which is about ~5 x 10^4 while the dielectric constant of pellets exhibit high value which is about ~1.4 x 10^5 with lower dielectric loss of ~0.16 at 1 kHz and room temperature. They reported that the differences between type of pellets and thick films presented might be due to the difference in grain size due to CuO contents which is different between both materials, and might be due to the different reactivity of the materials.

Through wet chemical method or sol-gel method, Yeoh et al. (2007) discussed the CCTO samples prepared by sol-gel method with high excess of Cu content. There is sudden increase in the dielectric for the sample prepared under pH 13. They proposed that it could be related to the way that the rich phase of Cu is distributed at the grain boundaries of the CCTO. The Cu segregation in the materials of the extra electron from the oxygen deficiency might reduce the Ti^{4+} to Ti^{3+}. It is suggested that this Cu segregation which caused the Ti^{4+} reduction

causing the resistivity reduction and the formation of an n-type semiconducting material.

Zhao et al (2012) also reported the employment of the sol-gel synthesis to obtained nano-size powder. By sintering the samples at 1125 ^{o}C, CCTO material with excellent dielectric properties were obtained. By increasing the sintering temperature from 600 to 900 ^{o}C, the crystalline peaks obtained from X-ray diffraction analysis becomes stronger and stronger. The impurity phases of CuO and TiO_2 completely disappeared when the calcinations temperature reached 900 ^{o}C and pure CCTO powders were obtained with cubic structure.

Moreover, Thomas et al. (2008) reported that the nano-crystalline structure of CCTO pure phase ranging from 30 to 200nm can be obtained when heat treated at temperature above 680 ^{o}C. They reported that the evolution of CCTO phase with increasing temperature of annealing is associated with the changing stereochemistry of Cu(II) ions from distorted octahedral to squashed tetrahedral and further to square-planar coordination.

2.6 The Effect of Dielectric Properties via Doping Schemes

Generally, the doping agent or dopant is normally inserted into a substance in very low concentrations in order to alter the electrical or dielectric properties of the substance. The atoms of the dopant addition very commonly take the place of the elements that has lower differences in the ionic radii. There have been a number of studies about the doping effects on the dielectric properties in this material. It was

revealed that the doping method will improved the dielectric constant and loss tangent such as CCTO modified by $SrTiO_3$, and also Cr_2O_3 doped CCTO ceramics (Kwon et al., 2008; Yu et al., 2008). In the Ti-deficient CCTO, the similar improvement in dielectric properties was also found. Compared with the stoichiometric ceramics $CaCu_3Ti_{4.0}O_{12}$, Ti-deficient ceramics $CaCu_3Ti_{3.9}O_{12}$ have the larger lattice parameter, the higher force constant, and smaller dielectric constant and the lower dissipation factor, although their fundamental characters of dielectric response are similar (Chen et al., 2007).

On the other hand, a Mn doping study by Li et al. (2006), was focused on the origin of semiconductivity in $CaCu_{2.94}Mn_{0.06}Ti_4O_{12}$ in terms of a cation non-stoichiometry model. It was found out that Mn-doped CCTO increases the bulk resistivity by six orders of magnitude higher than CCTO via impedance analysis. They suggested that different compositions in grains and grain boundaries may cause the suppression of bulk conductivity in Mn-doped CCTO. In this study, a lot of researchers reported that CCTO have perovskite structures and high-dielectric constant, but they have distinct mechanisms for the dielectric properties (Yu et al., 2008; Bender and Pan, 2005).

There are few reports been reported on how the doping will affect the properties of the CCTO thin film material. Saji and Choe (2009) reported that the yttrium doping affect the dielectric properties of the CCTO materials. They reported that the dielectric constant increase marginally with the increasing amount of yttrium dopant with low loss factor of about ~0.06 at 1 kHz. The substitution of the yttrium into the CCTO materials seems to reduced the dielectric constant of

high frequency reduction and also increased the low frequency dielectric relaxation which is suggested to be due to the conductive grains.

Moreover, the La doping study by Jin et al. (2009) through sol gel method of CCTO thin films shows that the appropriate introduction of La into CCTO materials results in flat dielectric constant values. There are inconsistent values of the dielectric constant with the increasing of the La amount. They reported that the samples with La doping of X = 0.05-0.20 result in smaller dielectric value than sample with 0.00 La (undoped sample). However as the maximum dielectric constant of CCTO thin film was obtained as the X = 0.20 which is also higher than CCTO with zero dopant. This conductivity phenomenon might be explained by the alternative mechanism of the CCTO which is known as oxygen loss mechanism according to "$O^{2-} \rightarrow Vo + ½\ O_2 + 2e^{-}$" as reported by Morrison et al., (2001).

La^{3+} typically has high coordination character of the materials. According to Eriksson et al., (1979), the lanthanum nitrate hexahydrate $[La(NO_3)_3(H_2O)_5]$ is comprised of discrete pentaaquatris (nitrato) lanthanum(III) complexes and water of hydration. It is also surround with the complex hydrogen bonds network. The lanthanum nitrate hexahydrate was used to substitute into the CCTO material as the La^{3+} ions radius are so close in value in which the La^{3+} has 1.15 Å whereas the Ca^{2+} has 1.05 Å ions radius which explained the reason of why La^{3+} is preferable to be substitute with the Ca^{2+}. Table 2.1 shows the properties of dopant, La that are going to be used in the research. A view of the $[La(NO_3)_3(H_2O)_5]$ complex is presented in Figure 2.4, which also shows the labeling of the atoms. There are 11-coordinate polyhedrons around the central La atoms. Six of the coordination sites are occupied

by three bidentate nitrate groups, and the remaining five ligands are water molecules as reported by Eriksson et al., (1979).

Table 2.1: Properties of Lanthanum Nitrate Hexahydrate

Properties	
Molecular formula	$[La(NO_3)_3(H_2O)_5]$
Molar Mass	433.01 g/mol
Appearance	White crystalline solid
Odor	Odorless
Melting Point	65-68 °C
Boiling Point	126 °C
Crystal Structure	triclinic
Space Group	P1bar
Coordination	11-coordination complex

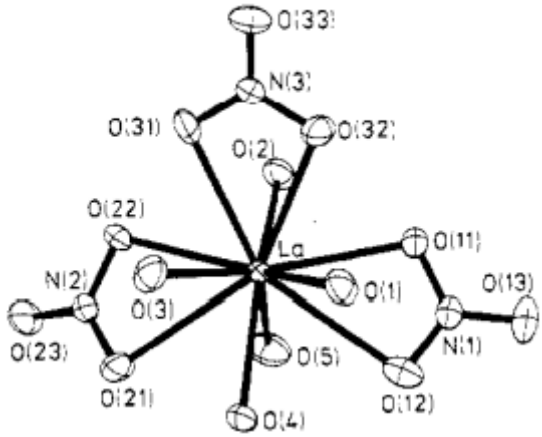

Figure 2.4: Perspective view of the $[La(NO_3)_3(H_2O)_5]$ complex with atomic numbering. (Eriksson et al., 1979)